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# Electron Diffraction Study of Trifluoromethyl Iodide†

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A reinvestigation of $CF_3I$ by electron diffraction for this molecule has confirmed the complex atomic scattering factors of Ibers and Hoerni. The structural parameters agree with those reported from earlier, inconclusive determinations.

THIS is the second of a series of new electron diffraction studies of molecules containing both heavy and light atoms. The background of these studies has been given in the preceding article on tetramethyl lead,[1] and will not be repeated here. The major purposes of the present work were to obtain a check on Ibers and Hoerni's calculation of complex atomic scattering factors for electron diffraction[2] and to study the structure of $CF_3I$.

The structure of $CF_3I$ had already been studied both by the microwave method[3] and by electron diffraction[4]; however, we could hardly be satisfied with the reported results. In the microwave investigation, only one moment of intertia was measured, thus establishing one constraint on the three structural parameters. In the electron diffraction report, there was a disquieting lack of any evidence of the large phase-shift effects to be expected on the basis of Ibers and Hoerni's calculations, or even of Schomaker and Glauber's first paper.[5] Moreover, the parameter determination was carried out in an unreasonable way that made the final results depend on the accident of just which intensity curves happened to be calculated as well as on the details of the diffraction pattern.[6]

## EXPERIMENTAL

Two sets of photographs, both made with our new apparatus, were used: a set of nonsector photographs made in 1954 on Kodak-50 plates with a sample prepared from trifluoroacetic acid, and a set of sector photographs made in 1956 on Kodak Process plates with a sample obtained from the Caribou Chemical Company. The camera distance and wavelength (checked against zinc-oxide photographs[7]) were 9.627 cm (both sets), 0.0619 A (nonsector set), and 0.0627 A (sector set). The sector was approximately an "$r^3$" sector, with angular opening $\alpha$ proportional, except near the center, to radius $r$ cubed.

## DIFFRACTION PATTERN

Visible rings extend to about $q=80$ on the nonsector pictures and to the edge of the sector ($q\sim150$) on the sector pictures, although the outer rings are so weak that no measurements of diameters were attempted beyond $q\sim100$. In marked contrast to Bowen's report, the pattern (curves C. W. and V. S., Fig. 1) clearly shows effects of the heavy-atom, light-atom cutoffs, becoming prematurely weak at about ring 5 and from there on out showing no agreement in detail with any intensity curve, either Bowen's or ours, calculated without the phase-shift factors.

It seems possible that Bowen's observations are to be explained on two grounds: first, that he greatly overestimated the strengths of the weak but comparatively sharp maxima 5 and 6, as indeed befits their appearance if not their proper interpretation; and, second, that his pictures may have been so weak beyond ring 8 as to vitiate the succeeding observations. His $s_{obs.}$ values agree well with ours through ring 8 but then rapidly lag behind and for the last two rings are almost exactly out of phase, as is perhaps consistent with the above suppositions. It does not seem possible that Bowen's pattern was actually much different from ours, even though the wavelength used may, according to his report, have been as low as 0.05 A: the dependence of the phase-shifts on electron energy is not very rapid in any case and for $CF_3I$ at 40 kev is, according to Ibers and Hoerni's approximate extrapolation formula, almost entirely negligible. Furthermore, one of their exact check calculations, being for $Z=60$, $V=55$ kev, happens to be relevant, and leads to the same conclusion.

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[1] C. Wong and V. Schomaker, J. Chem. Phys. **28**, 1007 (1958).
[2] J. A. Ibers and J. A. Hoerni, Acta Cryst. **7**, 405 (1954).
[3] J. Sheridan and W. Gordy, J. Chem. Phys. **20**, 591 (1952).
[4] H. J. M. Bowen, Trans. Faraday Soc. **50**, 444 (1954).
[5] V. Schomaker and R. Glauber, Nature **170**, 290 (1952).
[6] Because of this error of method, all of Bowen's results must be held in question. An example of a doubtful result is his aberrant value of 109.5° for ∠ FCF in $CF_3Br$, for which he happened to have two satisfactroy curves of total "weight" 3 at ∠ FCF = 112.5° but only one of "weight" 1 at 104.5°, besides several at 108.5°. However, his acceptance of curve 6 at 112.5° (Fig. 4, p. 448) is itself most questionable, since this curve disagrees strongly with his visual curve in showing max 3 much weaker than the average of max 2 and 4, and min 6 (Bowen's numbering) much too strong.
[7] See K. Hedberg and A. J. Stosick, J. Am. Chem. Soc. **74**, 954 (1952).

Our visual curves were drawn in the usual way from observations on both sets of photographs; they need some special explaining, however, because the sector, it was eventually realized, had serious irregularities of contour that almost completely invalidated the original interpretations (curves C. W. and V. S.) in the region $33<q<53$. The sector calibration function, $r^3/\alpha$, has a rather sharp peak at $q\sim46$ amounting to 1.6% and a smaller, sharper peak at $q=38$. The corresponding corrections (shown dashed) are highly uncertain: for C. W., who had based this part of his curve entirely on the sector pictures, the corrections are very large and accordingly unreliable (maximum 6, by the best theoretical curves, has an amplitude, above and below the general trend of minima 6 and 7, of only about 0.1% of the underlying background intensity); for V. S., who for no good reason had drawn a compromise between the differences in the sector and nonsector patterns, an exact definition of the compromise is impossible. We rely instead on the curves (a), which were drawn late in the course of the work from the nonsector pictures only.

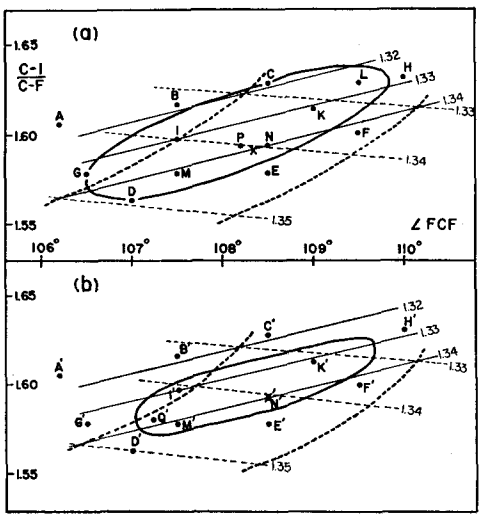


FIG. 1. Electron diffraction curves for $CF_3I$. Visual curves: for detailed explanation see text. Calculated curves: the models are defined below.

| Curve | C—I/C—F | ∠ FCF | $\delta_{FI}$ (A) | $\delta_{CI}$ (A) |
|---|---|---|---|---|
| $B$ | 1.617 | 107.5 | 0.08 | 0.08 |
| $C$ | 1.629 | 108.5 | 0.08 | 0.08 |
| $C_1$ | 1.629 | 108.5 | 0.09 | 0.10 |
| $E$ | 1.579 | 108.5 | 0.08 | 0.08 |
| $G$ | 1.579 | 106.5 | 0.08 | 0.08 |
| $I$ | 1.598 | 107.5 | 0.08 | 0.08 |
| $L$ | 1.629 | 109.5 | 0.08 | 0.08 |
| $L_1$ | 1.629 | 109.5 | 0.07 | 0.07 |
| $N$ | 1.594 | 108.5 | 0.08 | 0.08 |
| $N'$ | 1.594 | 108.5 | 0.09 | 0.094 |

| Curve | $a_{F\cdots I}$ ($10^{-4}$ A$^2$) | $a_{C-I}$ ($10^{-4}$ A$^2$) | $a_{F\cdots F}$ ($10^{-4}$ A$^2$) |
|---|---|---|---|
| $B$ | 10 | 5 | 5 |
| $C$ | 20 | 16 | 16 |
| $C_1$ | 20 | 16 | 16 |
| $E$ | 10 | 5 | 5 |
| $G$ | 10 | 5 | 5 |
| $I$ | 10 | 5 | 5 |
| $L$ | 20 | 16 | 16 |
| $L_1$ | 20 | 16 | 16 |
| $N$ | 10 | 5 | 5 |
| $N'$ | 10 | 5 | 5 |

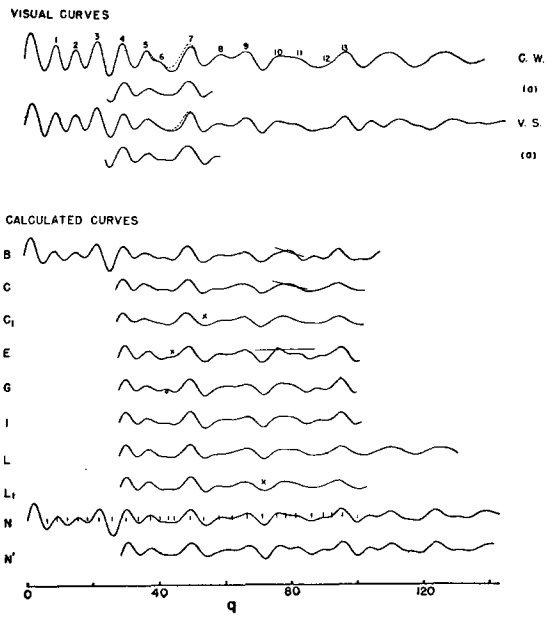


FIG. 2. Parameter maps for $CF_3I$. (a) For $q_{FI}^0=q_{CI}^0=62.5$ —"space $A$". (b) For $q_{FI}^0=55.5$. $q_{CI}=53$—"space $B$". Light lines: microwave C—F contours. Light dashed lines: electron-diffraction C—F contours. Heavy lines: range of acceptability of shape parameters. Heavy dashed lines: range of agreement of E.D. and MW contours; see text.

## RESULTS AND DISCUSSIONS

Five parameters of the $CF_3I$ model, namely, the shape parameters <FCF and C—I/C—F and the differential vibration parameters $a_{FI}$, $a_{CI}$, and $a_{FF}$ were varied in the theoretical intensity calculations, the distance C—F being regarded as the size parameter. The complex atomic scattering factors given by Ibers and Hoerni[2,8] were used for all atoms but were modified for most of the curves by varying the two phase-shift parameters[1] $q_{FI}^0$ and $q_{CI}^0$. Some of the curves are shown in Fig. 1, and most of them are defined in Fig. 2, which represents two sections in our parameter space.

The FI cutoff, $q_{FI}^0$, is primarily determined by the shapes of maxima 8 and 9 and minima 8 and 10, which

[8] Both the Ibers-Hoerni scattering amplitudes and the Born-approximation amplitudes, $f^B=(Z-f_{x\ ray})/s^2$, were satisfactory for this work, whereas the conventional approximation $f=Z/s^2$ was unsatisfactory. With it max 6, for example, becomes very much too strong, and min 6 becomes too deep and symmetrical. Bowen's best curve, No. 5, Fig. 5, illustrates this very well. Recalculated with the Ibers-Hoerni amplitudes—but without their phase-shifts—it agrees with Bowen's visual curve in regard to the asymmetry of max 5, which none of his curves as presented do, and has the strength of max 6 about halved.

TABLE I. Observed $q$ values and quantitative comparison for curve $N$.

| Rings | Minimum $q_0$[a] | Minimum $q_N/q_{obs}$ | Minimum $W$. | Maximum $q_0$[a] | Maximum $q_N/q_{obs}$ | Maximum $W$. |
|---|---|---|---|---|---|---|
| 1 | 6.23 | 0.949[b] | 0 | 9.13 | 0.997[b] | 0 |
| 2 | 12.10 | 1.017[b] | 0 | 15.12 | 1.025[b] | 0 |
| 3 | 18.12 | 1.010 | 1 | 21.50 | 1.023 | 3 |
| 4 | 25.36 | 1.021 | 6 | 29.79 | 1.014 | 8 |
| 5 | 33.47 | 1.007 | 10 | 37.29 | 0.982 | 5 |
| 6 | 40.10 | 0.997[b] | 0 | 42.65 | 1.001[b] | 0 |
| 7 | 44.35 | 1.003[b] | 0 | 49.35 | 1.003 | 10 |
| 8 | 53.33 | 1.016 | 10 | 57.90 | 1.014 | 2 |
| 9 | 62.07 | 0.994 | 2 | 66.45 | 1.006 | 8 |
| 10 | 71.00 | 1.010 | 10 | 75.34 | 1.013 | 2 |
| 11 | 78.04 | 1.015 | 1 | 81.23 | 1.006 | 1 |
| 12 | 86.01 | 1.000 | 1 | 89.53 | 1.000[b] | 0 |
| 13 | 92.10 | 0.992[b] | 0 | 95.32 | 0.999 | 7 |
| 14 | 100.41 | 0.994 | 3 | | | |

Weighted av: 1.007; C—F = 1.007 × 1.330 = 1.339 A.
Unweighted av: 1.007; av. dev., 0.008.

[a] Average of C.W. and V.S.
[b] Not included in the unweighted average.

are comparatively insensitive to all the other parameter variations. For a good fit to the visual curve, $q_{FI}^0 \sim 60$ is required: with $q_{FI}^0 < 52$ minimum 8 becomes too broad, and maximum 8 shifts outward from the observed position; with $q_{FI}^0 > 67$ minimum 10 becomes too broad and weak, and maximum 9 is deformed. The best choice is perhaps $q_{FI}^0 = 59$ with limits of $\pm 5$. The CI cutoff is less well determined, being weakly coupled, in effect, with $a_{C-I}$ and $\angle$FCF; on the other hand, the theoretical prediction[2,9] $q_{FI}^0 < q_{CI}^0$ is almost certainly correct. Altogether, for the range of $\angle$FCF and the value of $a_{CI}$ established below, our conclusion is $q_{CI}^0 = 55 \pm 8$. Curves $C$, $C_1$, $L$, $L_1$, $N$, and $N'$, selected from the many calculated in this part of the investigation, may be used to follow the foregoing description.

The differential vibration parameters,

$$a_{ij} = (\langle \Delta r^2_{ij} \rangle - \langle \Delta r_{CF}^2 \rangle)/2,$$

were not varied systematically; instead, $a_{F\cdots I}$ and the average of $a_{F\cdots F}$ and $a_{C-I}$ were deduced rather directly from the observed pattern, and, in the absence of any contrary indication, $a_{F\cdots F}$ and $a_{C-I}$ were assumed equal. The values so obtained, $a_{F\cdots I} = 0.0010$ A$^2$ and $a_{F\cdots F} = a_{C-I} = 0.0005$ A$^2$, are in agreement, according to rough calculation, with the observed vibrational frequencies.[10] The shape parameters were varied rather widely in the course of the cutoff study and were finally varied systematically for two sets of $q^0$ values close to the final choices 59 and 55 cited previously. For the first set, $q_{FI}^0 = q_{CI}^0 = 62.5$—"space $A$", the following considerations apply. Maximum 6 grows larger in curves $D$,[11] $B$, $I$, $G$,[11] and $A$; it moves into maximum 7 on curves $E$ and $F$.[11] On curves $D$, $E$, and $F$ maximum 10 is too strong relative to maxima 9 and 13. Maximum 11 is higher than maximum 10 on curves $A$, $B$, $C$, $L$, and $H$.[11] The position of minimum 9 is very much shifted toward maximum 9 on curve $G$. Accordingly, the range of acceptability of the shape parameters is that shown in Fig. 2(a). For curves inside this range, such as $L$, $I$, and $N$, agreement with the visual curves is good. For the second set of $q^0$ values, $q_{FI}^0 = 55.5$ and $q_{CI}^0 = 53$—"space $B$," the important considerations are similar, with the addition of the shape of minimum 8, which is here more sensitive to the shape parameters. The range of acceptability [Fig. 2(b)] is much smaller than for space $A$.

The usual quantitative comparison of observed and calculated $q$ values is given in Table I for one of the best curves, $N$, and is summarized in Table II for most of the curves of spaces $A$ and $B$. A refinement of the shape determination is made possible by the microwave value[3] for the larger moment of inertia, which defines C—F as the function of C—I/C—F and $\angle$FCF indicated by solid contours in Fig. 2. Corresponding electron diffraction contours, plotted from Table II, are shown lightly dashed, and the limits beyond which the discrepancy exceeds 0.01 A (perhaps only 0.005 A should be allowed) are shown by heavy dashes. The over-all range of acceptability is accordingly narrowed and shifted in the direction of larger $\angle$FCF. On the other hand, the average deviations quoted in Table II, although all satisfactory, tend to be smallest for somewhat smaller C—I/C—F so that points $X$ and $X'$, rather than the centers of the ranges of acceptability derived originally from qualitative considerations alone, were chosen for the best models in spaces $A$ and $B$. Fortunately, $X$ and $X'$ differ very little (0.2° in $\angle$FCF and 0.002 in C—I/C—F); we therefore take their average for the best model and ignore the very small effect on the shape parameters of any error in $q_{FI}^0$ and $q_{CI}^0$. Discarding the electron diffraction size determination in favor of the highly precise microwave determination, reading off estimated limits of error from Fig. 2, and summarizing the $q^0$ and $a$ values, we then

TABLE II. Summary of quantitative comparisons of observed and calculated $q$ values.

| Space $A$ Curve | C—F[a] | Av dev.[b] | Space $B$ Curve | C—F[a] | Av dev.[b] |
|---|---|---|---|---|---|
| $B$ | 1.334 | | $B'$ | 1.334 | |
| $C$ | 1.325 | | $C'$ | 1.327 | |
| $D$ | 1.349 | | $D'$ | 1.350 | |
| $E$ | 1.343 | | $E'$ | 1.344 | |
| $F$ | 1.335 | | $F'$ | 1.337 | |
| $G$ | 1.346 | | $G'$ | 1.345 | |
| $H$ | 1.323 | | $H'$ | 1.325 | |
| $I$ | 1.341 | 0.009 | $I'$ | 1.341 | 0.011 |
| $K$ | 1.331 | 0.010 | $K'$ | 1.332 | 0.009 |
| $L$ | 1.327 | | | | |
| $M$ | 1.343 | 0.008 | $M'$ | 1.345 | 0.010 |
| $N$ | 1.339 | 0.008 | $N'$ | 1.341 | 0.008 |
| $P$ | 1.339 | 0.008 | | | |
| | | | $Q'$ | 1.345 | 0.010 |

[a] From weighted average, see Table I.
[b] From unweighted average, see Table I.

[9] R. Glauber and V. Schomaker, Phys. Rev. **89**, 667 (1953).
[10] S. R. Polo and M. K. Wilson, J. Chem. Phys. **20**, 1183 (1952).
[11] Not illustrated in Fig. 1.

Table III. Structural parameters for trifluoromethyl iodide.

| | a | b | c | d |
|---|---|---|---|---|
| ∠FCF,° | 108.4(+1.4–1.9) | 108.2±1.6 | 108.3±2 | 108±1 (assumed) |
| C—I/C—F | 1.593(+.046–.029) | 1.602±.038 | 1.598 | 1.602 |
| C—F, A | 1.340(+.009–.021) | 1.334±.015 | 1.328±0.026 | 1.332 (assumed) |
| C—I, A | 2.135(+.033–.031) | 2.137±.032 | 2.122±0.037 | 2.134±0.011 |

[a] Electron diffraction plus moment of inertia from reference 3. See text.
[b] Similar to *a*; but E. D. size determination ignored. See text.
[c] Electron diffraction; reference 4.
[d] Microwave spectroscopy; reference 3.

have $q_{FI}^0=59\pm5$, $q_{CI}^0=55\pm8$, $a_{F\cdots I}=0.0010$ A$^2$, $a_{F\cdots F}=a_{C-I}=0.0005$ A$^2$ (equality assumed), and the values listed in column a of Table III.

It will be noted that the electron diffraction (E.D.) data and the microwave (MW) moment of inertia are in good but not perfect agreement, and that, partly in order to minimize the extent of disagreement, the diffraction shape determination was modified somewhat. If the diffraction size determination were completely ignored, and the shape determination accordingly based entirely on the original qualitative considerations (heavy solid curves in Fig. 2), the distance and angle values would be those listed in column b, Table III.

As Table III shows, our structural results are in remarkably good agreement with the earlier reports, both of which we had questioned. There is accordingly no occasion to change the previous discussions,[3,4] although it may be worthwhile to cite a few values for related molecules: $CF_3Cl$ (E.D.; ∠FCF=108.6±0.4°, C—F=1.328±0.002 A, C–Cl=1.751±0.004 A)[12]; (MW; ∠FCF=108.6±0.40°, assumed, C—F=1.328±0.002 A, C—Cl=1.748±0.009 A)[13]; $CF_3C{\equiv}CH$ (MW and E.D.; ∠FCF=107.5±1.0°, C—F=1.335±0.01 A)[14]; $CF_3H$ (MW; ∠FCF=108.48°, C—F=1.332 A)[15]; $CI_4$ (E.D.; C—I=2.12±0.02 A and 2.15±0.015 A)[16]; $CHI_3$ (E.D.; C—I=2.12±0.04A)[16]; $CH_3I$ (MW; C—I=2.139 A).[17] Our values for the cutoff points are in tolerable agreement with the theoretical values[2] $q_{FI}^0=57.5$ and $q_{CI}^0=51.0$.

[12] L. S. Bartell and L. O. Brockway, J. Chem. Phys. **23**, 1860 (1955).
[13] D. K. Coles and R. H. Hughes, Phys. Rev. **76**, 858 (1949).
[14] Shoolery, Shulman, Sheehan, Schomaker, and Yost, J. Chem. Phys. **19**, 1364 (1951).
[15] Ghosh, Trambarulo, and Gordy, J. Chem. Phys. **20**, 605 (1952).
[16] P. W. Allen and L. E. Sutton, Acta Cryst. **3**, 46 (1950).
[17] Miller, Aamodt, Dousmanis, Townes, and Kraitchman, J. Chem. Phys. **20**, 1112 (1952).